



Transparent Nanoporous Glass-Polymer Composite for U.S. Army Applications

**by Daniel J. O'Brien, Dr. Thomas F. Juliano, Parimal J. Patel,
and Dr. Steven H. McKnight**

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14. ABSTRACT This report explores the manufacturing of a novel transparent polymer-glass composite. The material is created by infiltrating nanoporous glass (Vycor, Corning Inc.) with different polymers. The Vycor pores (4–6 nm) are much smaller than the wavelength of light; thus, refractive index matching with the polymer is not necessary for transparency. Close to 90% of the pore volume can be filled by soaking the porous glass in methyl methacrylate and polymerizing in situ. The resulting composite is 95% transparent with excellent clarity, extremely low haze, and an elastic modulus that is well predicted by micromechanics.					
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1. Introduction

In order to field a more agile, survivable, and mobile fighting force, the U.S. Army is facing critical needs for lightweight, transparent armor material systems. Presently, to satisfy performance requirements, minimize weight, and maintain transparency, these systems consist of a laminated stack of materials with widely varying mechanical properties (figure 1). Each material is selected for specific functions and must also work as part of the system to defeat a given threat. In order for the laminate to work efficiently, stress waves must be transferred from one layer to the next (1, 2). When the stress wave crosses a dissimilar materials interface, a portion of the wave is reflected. The intensity of the reflection increases with the difference in the materials' acoustic impedances, Z , as shown in the following:

$$Z = \rho \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}} , \quad (1)$$

where ρ , E , and ν are the density, Young's modulus, and Poisson's ratio, respectively.

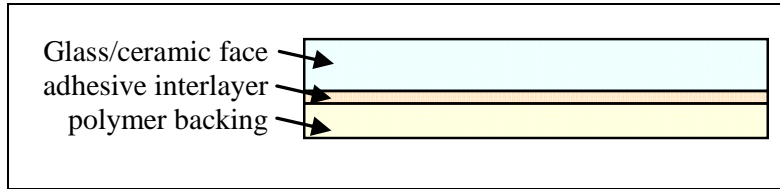


Figure 1. Schematic of simple transparent laminate.

The shock wave mitigation of laminated structures can be significantly improved through the gradual variation of Z through the structure's thickness. For systems not requiring transparency, polymer composites are a natural choice for such "intermediate Z " materials since matrix and reinforcement type, as well as relative volume fraction, may be chosen to engineer a wide range of impedance values. Unfortunately, composite materials are not typically transparent. In order to maintain transparency in traditional composites, constituent refractive indices must be precisely matched to better than one part in one thousand. Furthermore, due to the temperature dependence of the matrix refractive index, the composite is transparent over a relatively narrow temperature range. Newly developed clay- or nanofiber-based polymer nanocomposites are often transparent since the characteristic size of the reinforcement is much less than the wavelength of incident light. However, the volume fraction of reinforcement in these systems is very low and does not provide a significant increase in impedance over neat polymers. As such, a transparent intermediate impedance material does not presently exist. Micromechanical predictions suggest that an interpenetrating network of nanoporous glass and polymer should

produce such a material if it can be fabricated. This report explores the development of a novel transparent “intermediate Z” material by infiltrating nanoporous Vycor^{*} 7930 glass with appropriate polymers.

Vycor 7930 (figure 2) is manufactured from a soft alkali-borosilicate glass. Upon annealing at moderate temperature, the glass phase separates into two interpenetrating phases, one of which is rich in alkali and boric oxide. This phase is slowly leached away in a hot, dilute acid bath leaving behind a porous glass of ~96% silica (3). The process results in pores (4–6 nm) that are much smaller than the wavelength of light; thus, refractive-index matching with the polymer is not necessary to produce transparent composites (4).



Figure 2. Porous Vycor 7930 glass, 25 × 50 × 3 mm.

There is a considerable amount of literature on nanoporous glass such as Vycor. Typically, researchers use the material to study fundamental polymer thermodynamic transitions in confined spaces, for example (5–9). Lal et al. (8) studied the behavior of polystyrene chains in solution while confined inside nanoporous glass; Zarbin et al. (9) produced Vycor-polyaniline nanocomposites; and Mirau and Heffner (10) infused Vycor with polyethyl acrylate for nuclear magnetic resonance studies of the polymer confined in the pores. Vycor has also been used as a template material. Giunta et al. (11) infused Vycor with polyacrylonitrile in order to convert the glass-polymer composite to a carbon-silica composite through pyrolysis. Sotomayor et al. (12) used polyaniline-infused Vycor to produce a pH sensor, and Schnoes et al. (13) used polymer-filled Vycor as a holographic recording medium.

Although some authors have considered the infiltration of Vycor with polymers, to date, most of the studies have not considered the mechanical behavior of such a material. Abramhoff and Klein (14) studied the mechanical behavior of microporous glass-polymethyl methacrylate (PMMA) composites. Liu (15) performed an extensive study on the processing and properties of Vycor glass and found that with careful manufacturing the material is transparent. His study included characterizing the material’s properties including density, stiffness, strength, and thermal expansion coefficient, among others. Several years later, this effort was extended with a study on the mechanical properties of PMMA-impregnated porous glass over a range of volume fractions (16).

^{*}Vycor is a registered trademark of Corning, Inc., Corning, NY.

In this report, we will explore the processing and mechanical behavior of infused Vycor along with its optical properties to assess its viability as a component of a transparent armor laminate. A variety of characterization techniques, at the micro- and macroscale, are used to evaluate the Vycor-polymer composite.

2. Experimental Procedure

2.1 Processing

Three different monomers were considered for infiltration of the Vycor 7930 glass with 4–6 nm diameter pores: low-viscosity Spurr^{*} epoxy, isobornyl acrylate (IBA) (Sigma-Aldrich, St. Louis, MO), and methyl methacrylate 99% (MMA) (Sigma-Aldrich). Viscosity at room temperature for the Spurr epoxy is 60 cP, 2.6 cP for IBA, and 0.6 cP for MMA. The IBA and MMA monomers contained small amounts (10–200 ppm) of inhibitor (4-methoxyphenol) that was removed via an extraction process that was necessary to prevent material discolorations. The extraction process consisted of mixing the monomer once in a separation funnel with a 1% by weight NaOH solution (0.37M), followed by two rinses of deionized water, and concluded with a single rinse of brine solution to remove any water from the mixture. The Spurr epoxy was used as received.

Various geometry Vycor pieces, roughly 3 and 6 mm thick, were cleaned of any contamination through high-temperature treatment in a programmable temperature-controlled oven. Samples were first heated at a rate of 1 °C/min from room temperature to 80 °C and held for 2 hr to allow organic contaminants and any moisture to evaporate out. Next, the samples were heated to 600 °C at a rate of 1 °C/min, and this temperature was held for at least 24 hr before gradual cooling. Higher heating rates often resulted in catastrophic failure of the material through numerous internal cracks, perhaps due to nonuniform heating of the specimen, or as contaminants inside the pores boiled. Certain Vycor specimens were treated with a silane coupling agent (3-methacryloxypropyltrimethoxy silane, MPS) to improve bonding between the monomer and the Vycor. The silane solution was 1% MPS by weight in an ethanol/water solution (90/10, by weight) with pH adjusted to 4.5 using acetic acid. After stirring the solution for 1 hr, the Vycor was soaked for 30 min. Finally, the sample was removed from the solution and held at 95 °C for 1 hr to condense and crosslink the silane on the surface of the glass. After the cleaning process, the Vycor pieces were kept in a nitrogen environment until infiltration and polymerization.

Infiltration and curing procedures varied for each of the prepolymers. Samples soaked in Spurr epoxy at ambient conditions were allotted 3 days before curing the resulting pieces at 70 °C for 12 hr. Samples infiltrated with IBA and MMA were cured either with ultraviolet light or at

^{*}Spurr is a registered trademark of Polysciences, Inc., Warrington, PA.

temperatures near 60 °C for at least 12 hr. Benzoyl peroxide (BP) was used as a thermal initiator for the IBA- and MMA-filled samples.

The IBA processing schedule was as follows. First, either 0.5% or 1.0% by weight BP was dissolved into IBA. Next, to prevent oxygen inhibition of the free-radical polymerization, the resulting solution was bubbled with nitrogen gas in a vial for at least 20 min to remove any oxygen. A Vycor piece was placed in the vial, which was capped off to exclude any oxygen reentry. The samples soaked at room temperature for 24 hr, and then were placed in fresh nitrogen-bubbled IBA solution without initiator at 40 °C for 3 days. This ensured there was a suitable initiator concentration gradient in the material, with the initiator assisting to polymerize the sample from the inside first. In this way, as the material shrinks during polymerization, new monomer is available from the surrounding solution. Finally, the samples were removed from the solution and allowed to cure at 60 °C for 3 days. The final MMA infiltration processing schedule consisted of the following steps. First, 1.5% by weight BP was dissolved into the MMA and purged with nitrogen as before. The Vycor piece was placed into the solution for about 30 min, which was enough time for the MMA to completely saturate the pores (15). Next, the sample was placed in a nitrogen-bubbled 0.25% BP solution of MMA and polymerized in a convection oven for 3 days at 32 °C. As with the IBA sample, the specimen was transferred to a new polymer solution with reduced initiator concentration to promote polymerization from the “inside-out.” Finally, the samples were cured at 60 °C for 12 hr. After polymerization, excess PMMA was removed by cutting and grinding. To facilitate postprocessing, the Vycor pieces were placed between Teflon^{*} sheets for easier removal of excess PMMA. Before this final processing schedule, many different polymerization times and BP concentrations (from 0.05% to 3%) were attempted; however, results were not optimal.

2.2 Physical Property Characterization

To determine if the polymerization of MMA was affected by the nanoporous environment, the molecular weight of material polymerized inside the pores was compared to that polymerized outside the pores under the same conditions. In order to remove the PMMA from the pores, a 370-mg piece of infiltrated Vycor was submerged in 4-mL tetrahydrofuran (THF) overnight. After soaking the Vycor, it was dried at 90 °C for 6 hr and weighed to estimate the mass of PMMA leached out of the system. A small sample of PMMA that polymerized external to the Vycor was taken and dissolved in THF. The molecular weight of the samples was determined with gel permeation chromatography. As a comparison, a standard sample with a known molecular weight of 540 kD (Scientific Polymer Products, Ontario, NY) was also tested.

The density of the specimen was measured using Archimedes principle and the extent of pore filling was estimated using the rule of mixtures. The density of the glass phase was taken as 2.18 g/cm³, assuming the density of PMMA is 1.15 g/cm³, and the internal pore volume in the

^{*}Teflon is a registered trademark of E.I. DuPont de Nemours, Wilmington, DE.

Vycor is 28% (3). The optical quality (transmission, haze, and clarity) was assessed with a haze meter (Haz-gard Plus, Byk-Gardner, Columbia, MD).

Atomic force microscopy (AFM) was used to gather topographical information on cleaved surfaces of borosilicate Starphire* glass, unfilled Vycor, and PMMA-filled Vycor (see table 1). Images were obtained in tapping mode on a Digital Instruments Dimension 3100 Atomic Force Microscope (Veeco Metrology, Santa Barbara, CA).

Table 1. Density and fraction of pore volume filled for various polymer-Vycor composites.

Polymer	Composite Density (g/cm ³)	Fraction Pore Filled
Methyl methacrylate	1.85	0.87
Isobornyl acrylate	1.80	0.73
Spurr epoxy	1.63	0.19

2.3 Mechanical Property Characterization

Depth-sensing indentation was performed on Vycor specimens with a Nano Indenter XP (MTS Nano Instruments, Knoxville, TN). A total of 75, 5- μ m-deep indentations were made on three different Vycor samples, each polished to a 1- μ m finish. The first sample was unfilled porous Vycor, while the second and third were filled with PMMA. The third sample was also treated with silane prior to monomer infiltration. A cube corner indenter geometry was used to promote cracking around the impressions. Indentation strain rate was 0.1 s⁻¹ for all tests.

The tensile modulus of the filled specimens (20 \times 3.4 \times 1.7 mm) was measured under three-point bending using a dynamic mechanical analyzer (TA Instruments, New Castle, DE). The mechanical properties were also measured using ultrasonic wave speed. Specimens 3.5 mm thick were manufactured as described previously. Pulser-receiver transducers (Panametrics-NDT, Waltham, MA) were used to measure the longitudinal (transducer model V111, 10 kHz) and shear (transducer model V155, 5 kHz) wave speeds. The transducers were placed on the sample with a thin layer of honey to act as a coupling agent. The shear (G) and tensile (E) moduli were then calculated as follows:

$$G = \rho v_s^2, \quad (2)$$

and

$$E = \rho v_s^2 \frac{\left(3 \left(\frac{v_l}{v_s} \right)^2 - 4 \right)}{\left(\frac{v_l}{v_s} \right)^2 - 1}, \quad (3)$$

where ρ is the density and v_s and v_l are the shear and longitudinal wave speeds, respectively.

*Starphire is a registered trademark of PPG Industries, Pittsburgh, PA.

The modulus of rupture (MOR) was used to characterize the strength of the filled material, according to ASTM C158-02 (17). A 100- × 100- × 3.2-mm-thick plate was infiltrated with PMMA as described, and a surface grinder (FSG-3A1020, Chevalier Machinery, Santa Fe Springs, CA) was used to cut the plate into beams nominally 100 × 10 × 3.2 mm. After cutting, the beams were polished with progressively finer grit silicon carbide papers down to a final grit with a 6.5-μm average particle size. The specimens were observed with a polarimeter (PS100, Strainoptics, North Wales, PA) to assess the residual stress state. The MOR tests were conducted in four-point bending on a load frame (Synergie, MTS Systems, Eden Prairie, MN) fitted with a 500-N load cell. As shown in figure 3, the top and bottom spans were 55 and 85 mm, respectively. Eight samples were tested to failure at a constant displacement rate of 0.2 mm/min, and the MOR was calculated according to the ASTM standard with the beam equation for four-point bending, as follows:

$$MOR = \frac{3Pa}{bd^2}, \quad (4)$$

where P is the maximum load, a is the length of the moment arm span, b is the width of the specimen, and d is the thickness.

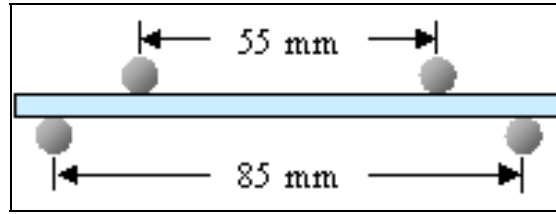


Figure 3. Schematic of MOR experiment.

To assess the toughness of the nanoporous composite, Izod impact (model 43-1, TMI Testing Machines, Amityville, NY) experiments were conducted on filled and unfilled specimens as well as borosilicate glass and neat PMMA. Both filled and unfilled specimens, 50 × 12 × 6.2 mm, were obtained by cutting 50- × 25- × 6.2-mm pieces of Vycor in half length-wise using a surface grinder. The filled specimens were manufactured by infiltrating and polymerizing MMA in the pores as described previously before rough grinding the excess polymer, cutting the filled material with the surface grinder, and finally, polishing the Izod specimen to 6 μm on all sides. After cutting and polishing, the unfilled specimens were cleaned as described previously to remove contaminants and excess water from the pores. To induce a more repeatable failure mode, before testing a 1-mm notch was carefully cut in the middle of the specimen with a 0.8-mm diamond saw. For comparison, glass and PMMA specimens of similar geometry were cut from 6.2-mm sheet using a water jet saw and band saw, respectively.

3. Results and Discussion

The feasibility of manufacturing a nanocomposite from nanoporous glass was first tested by infiltrating Vycor glass with various prepolymers (MMA, IBA, and a low-viscosity epoxy) after thorough glass cleaning and surface modification procedures. Table 1 shows the densities of the various specimens as well as estimates for the fraction of pores filled. We found that the epoxy used was too viscous to properly infiltrate the glass. The IBA filled the pores reasonably well; however, it resulted in specimens with a slightly yellowish tint and were difficult to process after curing.

Our most successful results occurred with MMA. These experiments showed that the nanoporous glass can be easily filled with the low-viscosity monomer at ambient conditions, as has been previously illustrated (15). The MMA saturates the nanoporous network in a few minutes by simply soaking the glass in the monomer. Optical clarity is maintained when polymerization proceeds slowly in excess monomer to allow diffusion of the monomer in the porous glass to offset shrinkage-induced voids within the sample. The process produces specimens with excellent optical quality (88.5% transmission, 7.9% haze, and 97.7% clarity, figure 4), near 100% pore filling with polymers possessing molecular weight similar to bulk polymerization.

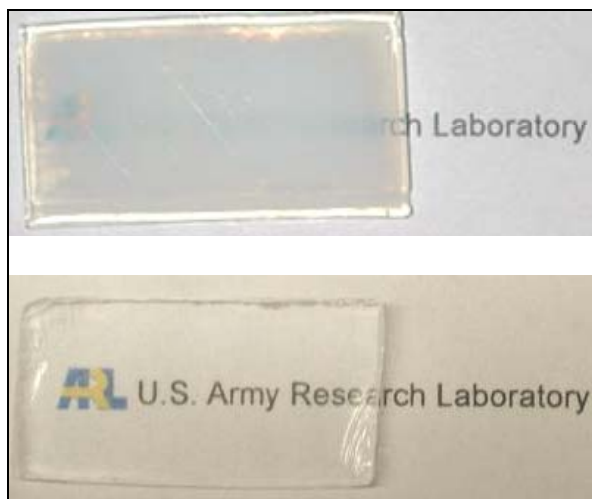


Figure 4. PMMA-filled Vycor specimens polymerized quickly outside of the solution (top) and polymerized slowly in solutions of decreasing initiator concentration (bottom).

As mentioned, the process is very sensitive to the rate of polymerization. Since the free-radical polymerization of MMA is easily inhibited by oxygen, it is important to design the process to minimize contact between ambient air and the monomer. For small samples, this is relatively easy because the sample can be polymerized in a small vial purged with N_2 through a septum. For larger samples, such as the 4×4 -in plates that were used to manufacture the four-point bend specimens, the specimens were placed in a petri dish, which was, in turn, placed in a bell jar that could be purged with N_2 . After purging, the entire vessel was placed in the oven for the polymerization cycle.

Through stress-induced birefringence, the polarimeter reveals information about the stress state of the specimen in the plane of the image. Figure 5 shows polarimeter images taken from the top and side of one of the MOR beams. In general, the image consists of two superimposed fringe patterns: isoclinic and isochromatic. The isoclinic fringes correspond to lines where the principle directions of the in plane stress field coincide with the axis of the polarizer, while isochromatics corresponds to lines of constant stress difference ($\sigma_1 - \sigma_2$). Since the top view in figure 5 is uniformly dark, we can conclude that the specimen is relatively free of residual stress in the plane. The side view, conversely, does reveal a fringe pattern through the thickness of the specimen that is not symmetric. The apparent stress field in the thickness direction could be a result of nonuniform infiltration and polymerization of MMA through the thickness. The asymmetry could be due to how the specimen was polymerized. For example, the layer of excess PMMA was thicker on one side of the specimen than the other, which could lead to polymerization shrinkage-induced bending of the plate. Or, the polymerization rate on one side might have been faster than the other due to oxygen inhibition and the increased exposure to air on one side of the specimen.

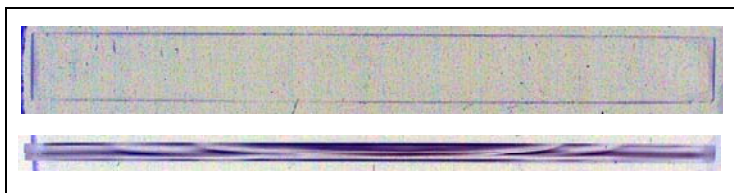


Figure 5. Polarimeter images of MOR specimens, top view (top) and side view (bottom).

AFM scans revealed that the cleaved texture of the filled and unfilled Vycor specimens (figure 6a) were much rougher than the Starphire glass (figure 6b). The surface of the Vycor specimens has a nodular texture with a feature size of ~ 100 nm in diameter. The rough nature of the cleaved surface could be an indication of a tortuous crack path that may result in greater energy absorption as compared to monolithic glass.

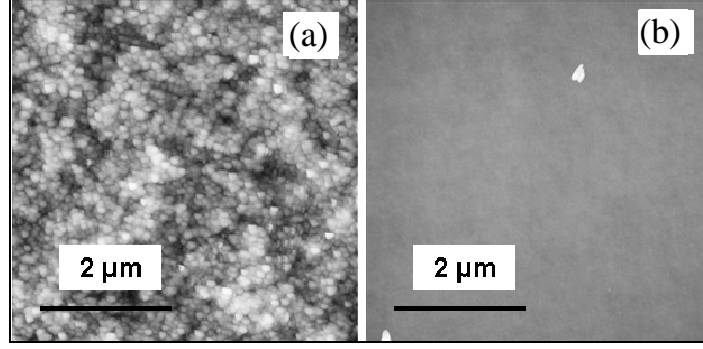


Figure 6. AFM topography scans of filled Vycor (a) and Starphire glass (b) cleaved surfaces. The height contrast scale in both images is 200 nm.

The mechanical properties of the resulting PMMA-infused materials were quantified with measurements at various length and time scales. Depth-sensing indentation showed that the Young's modulus of the porous material increased from 19 to 30 GPa for the silane and nonsilane treated samples. Indentation hardness of the filled samples was about 3.25 GPa compared to 2.00 GPa for the unfilled sample. Three-point bending shows an increase in modulus from 17 to 23 GPa, while ultrasonic measurements gave moduli of 15 and 29 GPa for unfilled and filled specimens, respectively. These results agree well with micromechanics calculations for composites consisting of two interpenetrating networks (18, 19), which predict a modulus of ~ 33 GPa for the Vycor-PMMA composite. The MOR for the PMMA-filled Vycor was 43.6 ± 4.6 MPa compared to 38.8 ± 5.0 MPa for a monolithic borosilicate glass tested under similar conditions. The impact toughness of the unfilled material was 0.09 ± 0.01 J/cm² and increased to 0.17 ± 0.02 J/cm² for PMMA-filled Vycor. By comparison, the impact toughnesses of monolithic borosilicate glass and neat PMMA were 0.07 ± 0.01 J/cm² and 0.44 ± 0.05 J/cm², respectively.

Most importantly, as table 2 shows, the acoustic impedance of the nanocomposite, at 7.8 kg/(m²-s), is an excellent intermediate value between that of a glass-ceramic face plate (14.8 kg/[m²-s]) and a polymer backing material (3.2 kg/[m²-s]).

Table 2. Properties of various transparent materials.

	Glass (Starphire)	Vycor-PMMA	PMMA	Vycor (unfilled)
Density (g/cm ³)	2.50	1.81	1.2	1.45
Young's modulus (GPa)	73.1	30	6.1	17
Acoustic impedance (kg/[m ² -s])	14.6	7.8	3.2	4.85

4. Conclusions

In this report, we explored the development of a new transparent material by infiltrating nanoporous glass with MMA and polymerizing the monomer in situ. Since the characteristic length of the reinforcement is much smaller than the wavelength of light, careful matching of constituent refractive indices is not necessary to maintain transparency. The material exhibits excellent optical properties and good mechanical properties with the elastic modulus well predicted by micromechanics. This nanocomposite material, with intermediate acoustic impedance, will provide transparent armor designers access to material properties not previously available and could lead to enhanced lightweight protection for the Soldier.

Future work will focus on the impact and ballistics properties of the nanoporous material by itself and as a part of a laminate. Figure 7 is an image of such a laminate. The laminate was constructed of 9-mm-thick borosilicate glass and 5-mm-thick polycarbonate with a 3-mm-thick Vycor-PMMA nanocomposite interlayer. Similar to the specimen shown in figure 8, the interlayer was only rough ground to remove the excess PMMA. In order to make the specimen transparent, the laminate was then bonded together using an epoxy with a refractive index very close to that of the Vycor-PMMA nanocomposite. The index-matched epoxy eliminated the scattering at the two interfaces, resulting in a transparent laminate (85.8% transmittance, 4.2% haze, and 93.9% clarity). This process shows that such transparent laminates can be manufactured.



Figure 7. Laminate of polycarbonate and borosilicate glass (9 mm) and polycarbonate (5 mm) with Vycor-PMMA interlayer (3 mm).

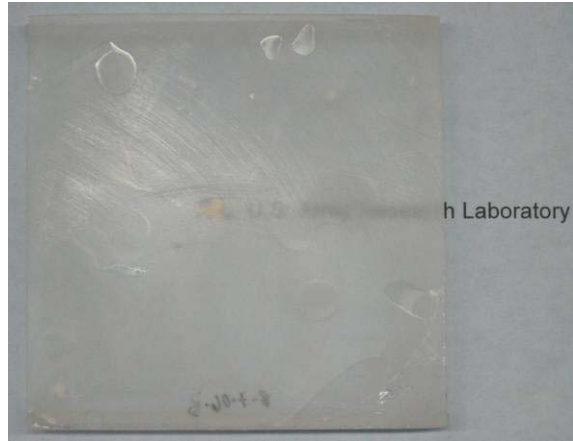


Figure 8. Vycor-PMMA composite plate after processing before incorporating into laminate using refractive-index matched adhesive.

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